

Metal-insulator transition in $\text{Sr}_{2-x}\text{La}_x\text{CoO}_4$ driven by spin-state transition

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We sought the origin of the metal-insulator transition in $\text{Sr}_{2-x}\text{La}_x\text{CoO}_4$, using electron-correlation corrected density functional calculations. Our results show that Sr_2CoO_4 is in an intermediate-spin (IS, $t_{2g}^4 e_g^1$) state and a strong Co^{4+} $3d$ - O $2p$ hybridization is responsible for its ferromagnetic metallicity. Upon La doping, however, a spin-state transition occurs in $\text{Sr}_{1.5}\text{La}_{0.5}\text{CoO}_4$: $\text{IS Co}^{4+} \times 2 + 1e \rightarrow \text{LS Co}^{4+} (t_{2g}^5) + \text{HS Co}^{3+} (t_{2g}^4 e_g^2)$ (LS: low spin; HS: high spin). Then the spin-state transition suppresses an electron hopping via a spin-blockade and gives rise to the insulating behavior of $\text{Sr}_{1.5}\text{La}_{0.5}\text{CoO}_4$. A corresponding superexchange accounts for its ferromagnetism. Thus, spin state could provide a way to tune materials properties.

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I. INTRODUCTION

It is quite common that a ferromagnetic (FM) material is metallic but an antiferromagnetic one is insulating (or semiconducting). Therefore, either a FM insulator or an antiferromagnetic metal seems to be an exception and would be of interest. In electron-correlated transition-metal oxides, charge, spin, orbital, and lattice degrees of freedom often couple to one another and result in abundant electronic and magnetic properties.¹ As a result, exceptions from the above ‘rule’ emerge more than rarely.² In this work, we will study such an exception — the FM semiconducting cobaltate $\text{Sr}_{1.5}\text{La}_{0.5}\text{CoO}_4$, and the end material of the $\text{Sr}_{2-x}\text{La}_x\text{CoO}_4$ series, Sr_2CoO_4 for a comparison.

$\text{Sr}_{2-x}\text{La}_x\text{CoO}_4$ is a group of interesting materials, which has the K_2NiF_4 -type layered structure. Sr_2CoO_4 is a FM metal,^{3,4} and it could even be a half metal.⁵ Upon La doping ($x=0.5$), $\text{Sr}_{1.5}\text{La}_{0.5}\text{CoO}_4$ turns semiconducting but remains FM.^{6,7} With La doping up to $x=1$, SrLaCoO_4 becomes a paramagnetic insulator.⁶⁻⁸ It is well known that cobaltates often have a spin-state issue. The spin state depends on Hund exchange, crystal field, and band hybridization, and it has a strong impact on the magnetic and electronic properties of cobaltates. It is this spin-state issue that has brought about a lot of debates in literature. Partially because of this, $\text{Sr}_{2-x}\text{La}_x\text{CoO}_4$ draw much attention very recently.⁹⁻¹⁷

In this work, using generalized gradient approximation plus Hubbard U (GGA+ U)¹⁸ calculations, we seek the origin of the metal-insulator transition induced by La doping in Sr_2CoO_4 , and pay attention to the FM semiconducting behavior of $\text{Sr}_{1.5}\text{La}_{0.5}\text{CoO}_4$. In Fig. 1, we sketch the Co $3d$ crystal-field levels in $\text{Sr}_{2-x}\text{La}_x\text{CoO}_4$ with a c -axis elongated CoO_6 octahedron. The electronic configurations are shown for an intermediate-spin (IS) state [Fig. 1(a)] and for a low-spin (LS) state [Fig. 1(c)] both relevant to a high-valent Co^{4+} ion. Our following GGA+ U calculations find that Co^{4+} in Sr_2CoO_4 favors the IS state, though somewhat modified compared to Fig. 1(a) due to hybridization effects and on-

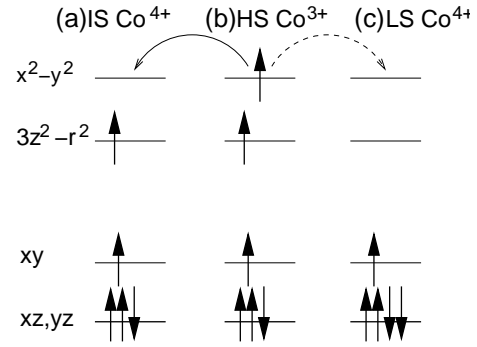


FIG. 1: Electronic configuration of (a) the IS and (c) LS state of a Co^{4+} ion in a c -axis elongated CoO_6 octahedron (a tetragonal crystal field), and of (b) the HS state of a Co^{3+} ion. While the x^2-y^2 electron would readily hop from the HS Co^{3+} to IS Co^{4+} via Zener’s double exchange, a hopping from the HS Co^{3+} to LS Co^{4+} is suppressed by a spin blockade. See more in the main text.

site Coulomb interactions, and that a strong Co $3d$ - O $2p$ hybridization results in FM metallicity of the compound. In Fig. 1(b), we show a high-spin (HS) state for a Co^{3+} , which emerges upon La doping. Here the Co^{3+} HS state is conceived, based not only on our very recent work about SrLaCoO_4 ,⁸ but also on a crystal-field scenario (see below). As SrLaCoO_4 has a Co^{3+} HS-LS mixed state,^{8,19} less La-doping in $\text{Sr}_{1.5}\text{La}_{0.5}\text{CoO}_4$ will most probably change the LS Co^{3+} into a LS Co^{4+} and leave the HS Co^{3+} unchanged, in order to maximize Hund exchange. Then $\text{Sr}_{1.5}\text{La}_{0.5}\text{CoO}_4$ would have the HS Co^{3+} and LS Co^{4+} ions. In this sense, upon La doping in Sr_2CoO_4 , there would be an IS-LS transition of the Co^{4+} ions, besides an introduction of the HS Co^{3+} ions. As seen below, our calculations indeed confirm this spin-state transition and find it to be the origin of the metal-insulator transition.

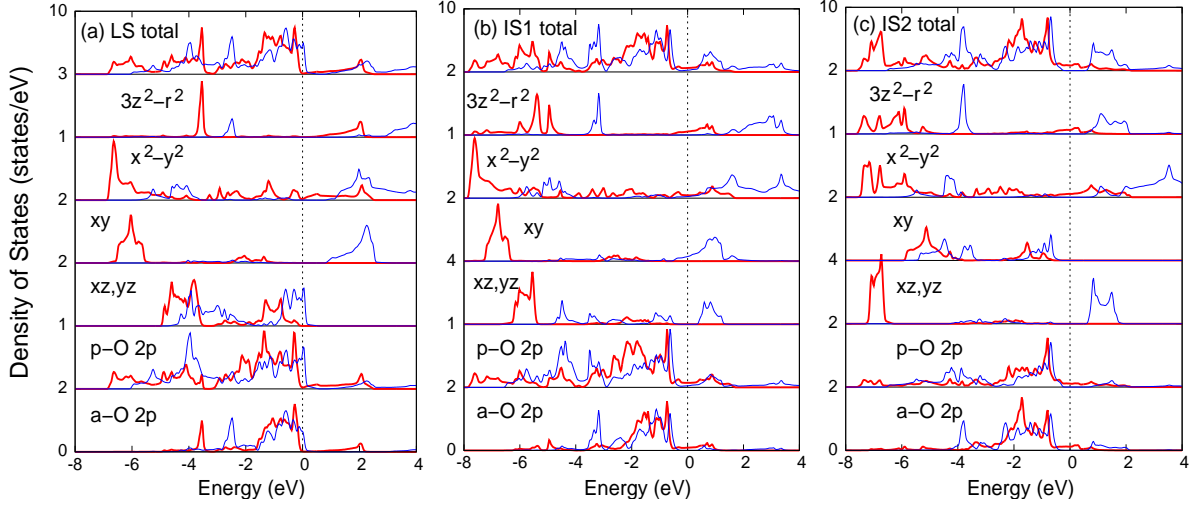


FIG. 2: (Color online) Total density of states (DOS), Co $3d$ -orbital resolved DOS, planar O (p-O) and apical O (a-O) $2p$ DOS of FM Sr_2CoO_4 in (a) LS, (b) IS1, and (c) IS2 states calculated by GGA+ U . The red (bold) curves stand for the up spin, and the blue (solid) for the down spin. Fermi level is set at zero energy. While the LS and IS1 states are metallic, the IS2 state is half metallic. The IS2 is the ground state, see also Table I.

II. CALCULATIONS AND DISCUSSION

We carried out GGA+ U calculations, using the full-potential augmented plane wave plus local orbital code (Wien2k).²⁰ The structural data were taken from Refs. 4 and 7. The muffin-tin sphere radii were chosen to be 2.5, 2.0, and 1.5 Bohr for (Sr,La), Co, and O atoms, respectively. A virtual atom with the atomic number $Z=38.25$ ($0.75Z_{\text{Sr}}+0.25Z_{\text{Y}}$) was used for the ($\text{Sr}_{1.5}\text{La}_{0.5}$) sites, as Sr and La(Y) ions are in most cases simple electron donors. The plane-wave cut-off energy of 16 Ry was set for the interstitial wave functions, and 1200 (600) \mathbf{k} points for integration over the Brillouin zone of Sr_2CoO_4 (of $\text{Sr}_{1.5}\text{La}_{0.5}\text{CoO}_4$ with a doubled unit cell). The spin-orbit coupling was included by the second-variational method with scalar relativistic wave functions. The typical value of $U=5$ eV and Hund exchange of 0.9 eV were used in our GGA+ U calculations to account for the electron correlation of the Co $3d$ states.^{8,19}

A. Sr_2CoO_4

We first calculated Sr_2CoO_4 . As seen in Table I, our configuration-state constrained GGA+ U calculations find three stable FM solutions, one LS and two IS states. Indeed, the IS states are more stable than the LS state. The LS state is metallic, see Fig. 2(a). The up-spin t_{2g} (xy and xz/yz) orbitals are fully occupied, and the down-spin xz/yz are almost fully filled. Note that owing to the high valence of the Co^{4+} ion and its negative charge-transfer energy,²¹ a strong $pd\sigma$ hybridization with the ligand oxygens bring about a large occupation on the e_g ($3z^2-r^2$ and x^2-y^2) orbitals. This accounts for the calculated total spin moment of $2.03 \mu_B/\text{fu}$ which is in-

creased from the formal LS $S=1/2$ state. The Co ion has a local spin (orbital) moment of 1.82 (0.09) μ_B within its muffin-tin sphere, see Table I.

Starting from the electronic configuration $t_{2g\uparrow}^3(3z^2-r^2)_{\uparrow}^1(xz+iyz)_{\downarrow}^1$ for the IS1 state, we also get a metallic solution with a total spin moment of $2.79 \mu_B/\text{fu}$. The up-spin e_g bands get almost doubly occupied due to the strong $pd\sigma$ covalency, and they cross Fermi level together with the down-spin xy band, see Fig. 2(b). The down-spin $xz+iyz$ (Y_{21}) orbital is fully occupied and well separated from the unoccupied $xz-iyz$ (Y_{2-1}) orbital. It is the $xz+iyz$ electron that contributes most to the calculated orbital moment of $1.02 \mu_B$. The local spin moment is $2.53 \mu_B$ for the IS1 Co ion.

The most stable IS state is achieved self-consistently from the initial configuration state $t_{2g\uparrow}^3(3z^2-r^2)_{\uparrow}^1xy_{\downarrow}^1$. It is FM half metallic, see Fig. 2(c). Only the up-spin e_g

TABLE I: The relative total energies ΔE (meV/fu) of FM Sr_2CoO_4 (SCO) in one LS and two IS states calculated by GGA+ U , the total spin moment M and the local spin/orbital moment of Co ions in unit of μ_B . A reference to figures is included. The corresponding data are listed for FM $\text{Sr}_{1.5}\text{La}_{0.5}\text{CoO}_4$ (SLCO). The Co^{3+} HS state is marked bold for clarity. Note that in our GGA+ U calculations, the IS Co^{4+} -IS Co^{3+} state converges to the LS-HS ground state.

SCO	ΔE	M (μ_B/fu)	Co^{4+} m_s/m_o		Fig.
LS	0	2.03	1.82/0.09		2(a)
IS1	-56	2.79	2.53/1.02		2(b)
IS2	-155	3.00	2.61/0.10		2(c)
SLCO	ΔE	M ($\mu_B/2\text{fu}$)	Co^{4+}	Co^{3+}	Fig.
IS-HS	0	7.00	2.85/0.13	2.89/0.85	3
LS-HS	-139	5.00	1.70/0.01	2.88/0.84	4

bands cross Fermi level. This solution has an integer spin moment of $3 \mu_B/\text{fu}$ as expected for the formal IS $S=3/2$ state. The Co^{4+} ion has a local spin (orbital) moment of 2.61 (0.10) μ_B , see Table I. This IS2 state is more stable than the LS state by 155 meV/Co and than the IS1 state by 99 meV/Co . As the xy singlet is a higher level than the xz/yz doublet in an elongated tetragonal crystal field, it seems a bit surprising that the IS2 state is more stable than the IS1 state. However, for the almost doubly occupied e_g orbitals [Figs. 2(b) and 2(c)], the planar x^2-y^2 orbital is itinerant but the $3z^2-r^2$ orbital is relatively localized. As such, a stronger Coulomb repulsion between the $3z^2-r^2$ and xz/yz electrons than that between $3z^2-r^2$ and xy makes the filling of the down-spin xy orbital energetically more favorable than that of the down-spin xz/yz . Apparently, the FM half-metallic solution of Sr_2CoO_4 is due to the significant $pd\sigma$ hybridization between the IS Co^{4+} ions and the planar oxygens. This is because the high-valent Co^{4+} ion has a negative charge transfer energy²¹ and thus its actual configuration is more like $\text{Co}^{3+}\underline{L}$. Indeed, Fig. 2(c) shows almost the $3d^6$ state of the HS Co^{3+} like and the ligand O $2p$ hole states. Moreover, the planar-O $2p$ hole state is more itinerant than the apical-O $2p$. As a result, the calculated spin moment of $0.03 \mu_B$ on the planar oxygen is smaller than that of $0.10 \mu_B$ on the apical oxygen.

B. $\text{Sr}_{1.5}\text{La}_{0.5}\text{CoO}_4$

Now we turn to the calculations for the $\text{Co}^{4+}\text{-Co}^{3+}$ mixed-valent $\text{Sr}_{1.5}\text{La}_{0.5}\text{CoO}_4$. As Co^{3+} ion has a larger radius than Co^{4+} , longer $\text{Co}^{3+}\text{-O}$ distances would produce a weaker crystal field for Co^{3+} , compared with Co^{4+} . In this sense, Co^{3+} could be in a higher spin state than Co^{4+} . Therefore, we first tested the IS $\text{Co}^{4+}\text{-HS Co}^{3+}$ state as a candidate for $\text{Sr}_{1.5}\text{La}_{0.5}\text{CoO}_4$. As seen in Figs. 1(a) and 1(b), the x^2-y^2 electron would readily hop from the HS Co^{3+} to IS Co^{4+} , giving rise to a FM half-metallic behavior via Zener's double exchange. This picture is indeed supported by our calculations, see Fig. 3: the up-spin x^2-y^2 bands both of the Co^{4+} and Co^{3+} ions are almost fully occupied but cross Fermi level due to the x^2-y^2 electron hopping and the strong planar $pd\sigma$ hybridization. This FM half-metallic solution has a total integer spin moment of $7 \mu_B/2\text{fu}$ as expected for the IS $\text{Co}^{4+}\text{-HS Co}^{3+}$ FM state ($S=3/2$ plus $S=2$). The formal HS Co^{3+} and IS Co^{4+} ions have, mainly due to the x^2-y^2 electron hopping, almost the same local spin moment (being about $2.9 \mu_B$ each), see Table I. Note, however, that this half-metallic solution disagrees with the experimental semiconducting behavior.^{6,7}

Taking into account the above crystal-field scenario, we then calculate the LS $\text{Co}^{4+}\text{-HS Co}^{3+}$ state, i.e., our calculations now involve a possible spin-state transition of the Co^{4+} ion from the IS state in Sr_2CoO_4 to the LS state in $\text{Sr}_{1.5}\text{La}_{0.5}\text{CoO}_4$. [This spin-state transition is likely upon La doping into Sr_2CoO_4 , as the introduced HS Co^{3+} ions

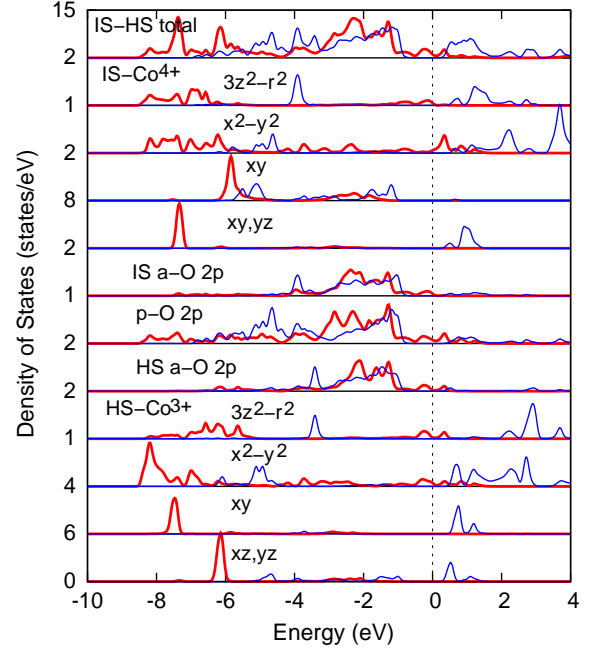


FIG. 3: (Color online) DOS of $\text{Sr}_{1.5}\text{La}_{0.5}\text{CoO}_4$ in the IS $\text{Co}^{4+}\text{-HS Co}^{3+}$ state calculated by GGA+ U . It is FM half metallic.

get bigger in size (compared with the IS Co^{4+} ions), and then a chemical pressure forces the IS Co^{4+} ions transit into the lower-volume LS state.] At a glance, an electron hopping from Co^{3+} to Co^{4+} is possible, as there could be no change of the electronic configurations (from the initial d^6+d^5 state to the final d^5+d^6 state). However, as seen in Figs. 1(b) and 1(c), the x^2-y^2 electron hopping from HS Co^{3+} to LS Co^{4+} is actually suppressed, particularly due to the spin-state issue. If such a hopping took place, there would be an energy cost of Hund exchange associated with the change of the spin states from LS-HS to IS-IS. As a result, the LS $\text{Co}^{4+}\text{-HS Co}^{3+}$ state will be stabilized at it is, and it has no real electron hopping (due to a spin blockade^{11,22}) and is thus insulating. However, a virtual hopping of the x^2-y^2 electron forth and back and the local Hund exchange would mediate a superexchange FM in the $e_g^0e_g^2$ configuration of the LS $\text{Co}^{4+}\text{-HS Co}^{3+}$ state.

The insulating but FM solution of the LS $\text{Co}^{4+}\text{-HS Co}^{3+}$ state is indeed confirmed by our calculations, see Fig. 4: it has a small insulating gap of about 0.3 eV . The $\text{Co}^{4+} t_{2g}$ orbitals carry a spin= $1/2$ (on the xy orbital), and the strong $pd\sigma$ hybridization brings about a large amount of e_g occupation and thus increases the local spin moment of the Co^{4+} to $1.7 \mu_B$, see Table I. The LS Co^{4+} ion has a negligible orbital moment of $0.01 \mu_B$. For the Co^{3+} ion, Co-O valency reduces its local spin moment to $2.88 \mu_B$. The total spin moment is $5 \mu_B/2\text{fu}$ as expected for this LS $\text{Co}^{4+}\text{-HS Co}^{3+}$ ($S=1/2$ plus $S=2$) state. In this semiconducting state, besides the localized t_{2g} and $3z^2-r^2$ orbitals, the x^2-r^2 orbital also gets localized due to the spin blockade. Then the formal HS Co^{3+} ion has

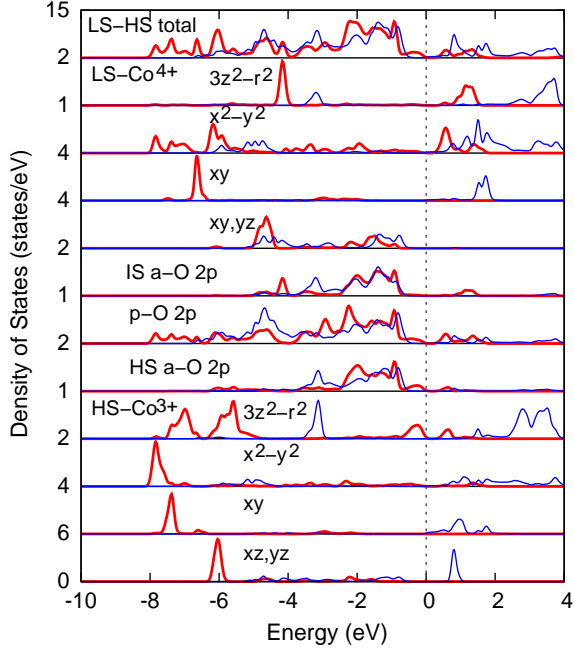


FIG. 4: (Color online) DOS of $\text{Sr}_{1.5}\text{La}_{0.5}\text{CoO}_4$ in the LS Co^{4+} -HS Co^{3+} ground state calculated by GGA+ U . It is FM semiconducting.

the configuration state $t_{2g\uparrow}^3 e_{g\uparrow}^2 (xz+iyz)_{\downarrow}^1$, i.e., the up-spin orbitals are fully occupied and form a closed subshell, but the rest single electron occupies the lowest crystal-field doublet xz/yz . As a result, the spin-orbit coupling lifts the orbital degeneracy, produces the Y_{21} ($xz+iyz$) complex orbital, and gives a large orbital moment of $0.84 \mu_B$ along the easy-magnetization c -axis. The importance of spin-orbit coupling was also demonstrated previously when studying the spin-orbital ground state of the perovskite LaCoO_3 .²³ Thus, in $\text{Sr}_{1.5}\text{La}_{0.5}\text{CoO}_4$ the total spin and orbital moments sum up to about $5.8 \mu_B/2\text{fu}$.

It is important to note that this LS Co^{4+} -HS Co^{3+} FM state is more stable than the above IS-HS FM state by 139 meV/fu . In addition, this LS-HS state brings about a local distortion against the homogeneous Co-O lattice measured so far in polycrystals. Our calculations doing atomic relaxations show that the LS Co^{4+} ion has the optimized Co-O bondlengths of $1.879 \text{ \AA} \times 4$ (in plane) and $2.011 \text{ \AA} \times 2$ (out of plane). The corresponding values are $1.911 \text{ \AA} \times 4$ and $2.061 \text{ \AA} \times 2$ for the HS Co^{3+} . Such atomic relaxations help the LS Co^{4+} -HS Co^{3+} state gain further an elastic energy of 54 meV/fu as shown by our calculations. The semiconducting electronic structure turns out to have insignificant changes due to the

atomic relaxations. For example, the local spin and orbital moments of the LS Co^{4+} (the HS Co^{3+}) are now 1.64 and 0.01 (2.92 and 0.83) μ_B , respectively (see Table I for a comparison). Moreover, our calculation finds a LS-HS ferrimagnetic solution to be less stable than the LS-HS FM solution by 34 meV/fu . The LS-HS ferrimagnetic solution has a total spin moment of $3 \mu_B/2\text{fu}$ as expected. The constituent LS Co^{4+} ($S = -1/2$) has a local spin (orbital) moment of -0.42 (-0.01) μ_B , and the HS Co^{3+} ($S = 2$) has 2.97 (0.84) μ_B . Furthermore, our calculations show that another possible spin state of $\text{Sr}_{1.5}\text{La}_{0.5}\text{CoO}_4$ —the IS Co^{4+} -IS Co^{3+} state is unstable and converges to the present LS-HS FM state. Therefore, the present FM semiconducting LS Co^{4+} -HS Co^{3+} solution is the ground state of $\text{Sr}_{1.5}\text{La}_{0.5}\text{CoO}_4$.

This FM semiconducting ground-state solution agrees with the experiments.^{6,7} Moreover, using the LS Co^{4+} -HS Co^{3+} state ($S=\frac{1}{2}$ and $S=2$ plus $L=1$), we estimate the effective magnetic moment

$$\mu_{eff} = \sqrt{0.5 \times 4 \times \frac{1}{2} \times \frac{3}{2} + 0.5 \times (4 \times 2 \times 3 + 1 \times 1 \times 2)} \approx 3.8 \mu_B/\text{Co}.$$

Taking a covalency reduction, this value is in good agreement with the measured one of $3.5 \mu_B$.⁶ Although the predicted magnetic moment of $2.9 \mu_B/\text{fu}$ (i.e., the above $5.8 \mu_B/2\text{fu}$) along the easy-magnetization c -axis (of a single crystal, ideally) is much bigger than the measured $1.5 \mu_B$,⁶ using of the polycrystals so far in the experiments would most probably account for the large reduction. The predicted LS-HS state, a big orbital moment along the c -axis, and the local Co-O distortions in $\text{Sr}_{1.5}\text{La}_{0.5}\text{CoO}_4$ call for further studies on a single crystal.

III. CONCLUSION

In summary, using GGA+ U calculations, we find that while Sr_2CoO_4 in the Co^{4+} IS ground state is a FM half-metal, $\text{Sr}_{1.5}\text{La}_{0.5}\text{CoO}_4$ has the LS Co^{4+} -HS Co^{3+} ground state. It is the Co^{4+} IS-LS transition that suppresses an electron hopping via a spin blockade and thus drives a metal-insulator transition in $\text{Sr}_{1.5}\text{La}_{0.5}\text{CoO}_4$. Moreover, the present spin-state picture consistently accounts for the FM behavior of metallic Sr_2CoO_4 via a $pd\sigma$ hybridization and that of semiconducting $\text{Sr}_{1.5}\text{La}_{0.5}\text{CoO}_4$ via a superexchange. Thus, spin state could provide a way to tune materials properties.

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